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Rho-axis-system Hamiltonian for molecules with one large amplitude internal motion

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The rho-axis system and the rho-axis-system Hamiltonian were devised and formulated to describe the rotational–internal–rotational motion of molecules possessing certain local geometrical symmetries. Nevertheless, they were employed to molecules without the required symmetries and apparently lying outside the range of their applicability. To justify such applications and to facilitate first-principles calculation of the corresponding spectroscopic parameters, the rho-axis-system and the rho-axis system Hamiltonian must be derived without assuming or imposing symmetry constraints. A derivation satisfying this requirement is described, and the rho-axis method is extended to molecules having a large amplitude internal motion of any kind. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1560634]

I. INTRODUCTION

Understanding the finer details of rotational–internal rotational dynamics, for instance in acetaldehyde (CH_3CHO), has been difficult due to, among various reasons, the deficiencies in our understanding of the Hamiltonians employed in the analysis of the experimental spectroscopic data. Some of these deficiencies have been described in Ref. 1. One of them, the problem of defining the torsional coordinate, has been solved in Ref. 2. Two other problems, which have not been solved yet, are the following:

The experimental rotational-torsional spectra of acetaldehyde[3,4] were fitted by a rho-axis-system (RAS) Hamiltonian derived by assuming a methyl group with three-fold symmetry.[5–8] Since the methyl group in acetaldehyde actually does not have have a C_3 symmetry axis,[9–11] the excellent fits obtained[3,4] might be surprising. Could a ρ-axis system Hamiltonian be derived without imposing symmetry constraints?

The first-principles calculation of spectroscopic parameters in a RAS Hamiltonian requires the transformation of an initial Cartesian molecule fixed system (MFS) of axes into the RAS.[1] However, the transformation to the RAS is not known except for the simple cases when a molecule with internal rotation has certain local geometrical symmetries.[5] Only a proof of existence of the RAS is known in the case of internal rotation in a molecule with asymmetric top and asymmetric frame.[12] Little is known about the transformation to the RAS in a molecule with a large amplitude internal motion (LAM) different from internal rotation.

This paper describes derivation of a transformation to the RAS and the RAS rotational-LAM Hamiltonian for a molecule with one LAM. The derivation involves no assumptions about local geometrical symmetries of the molecule. The results are obtained through an analysis of the properties of the transformation to the internal-axis system (IAS) and that of the corresponding IAS rotational-LAM Hamiltonian derived in Ref. 13.

II. PRELIMINARY CONSIDERATIONS

A simple prescription will be derived to transform a rotational-LAM Hamiltonian when the MFS is subjected to a rotation that may depend on the LAM coordinate.

The rotation of a molecule as a whole may be described by three Euler angles defining the orientation of a Cartesian MFS with respect to a Cartesian laboratory system (LS) of axes. The origin of the MFS is fixed to the center of mass of the molecule. Consider an initial MFS. Let the Euler angles φ, θ, and χ describe the orientation of the initial MFS with respect to the LS. Let $a_{\alpha,j}(\tau)$, $\alpha = x,y,z$, $j=1,2,\ldots,\mathcal{N}$, denote the coordinates of the atoms of the $\mathcal{N}$-atom molecule studied. The atom coordinates are functions of the LAM coordinate τ. Then, by rearranging the terms in the Hamiltonian derived by Pickett,[14] the rotational-LAM Hamiltonian operator may be written as

$$\hat{H}=\tfrac{1}{2}\hat{J}^t\mu_{RR}\hat{J}+\tfrac{1}{2}(\hat{p}-\{\hat{J}^t\omega\})\mu_{\tau\tau}(\hat{p}-\{\omega^t\hat{J}\})+V(\tau), \quad (1)$$

with

$$\mu_{RR}=I_{RR}^{-1}, \quad (2)$$

$$\omega=I_{RR}^{-1}I_{R\tau}, \quad (3)$$

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$$\mu_{\tau\tau}=(I_{\tau\tau}-\omega^t I_{RR}\omega)^{-1}, \tag{4}$$

$$I_{R\tau}=\sum_j m_j a_j \times \frac{\partial a_j}{\partial \tau}, \tag{5}$$

$$I_{\tau\tau}=\sum_j m_j \frac{\partial a_j}{\partial \tau}\cdot\frac{\partial a_j}{\partial \tau}, \tag{6}$$

where I_{RR} denotes the rotational tensor of inertia, a_j and m_j denote the column vector of the coordinates and the mass of the jth atom, respectively, $V(\tau)$ stands for the LAM potential energy function with the so-called pseudopotential energy terms incorporated, and superscript t means transposition. The column vector $\hat{J}$ contains the MFS components of the total angular momentum operator. They can be expressed in terms of the Euler angles φ, θ, and χ and the partial differential operators with respect to these angles.[15] $\hat{J}$ satisfies the commutation relation[15]

$$\hat{J}\times\hat{J}=-i\hbar\hat{J}. \tag{7}$$

The momentum operator $\hat{p}$ conjugated to the LAM coordinate is defined by

$$\hat{p}=-i\hbar\left(\frac{\partial}{\partial\tau}\right)_{\varphi,\theta,\chi}, \tag{8}$$

and it commutes with the MFS components of the total angular momentum operator, i.e.,

$$[\hat{J},\hat{p}]=\mathbf{0}, \tag{9}$$

where $\mathbf{0}$ is the zero vector $(0,0,0)^t$, since the Euler angles φ, θ, and χ are independent of τ.

The Schrödinger equation for $\hat{H}$ may be solved variationally for any given value of the total angular momentum quantum number J by using a direct product basis formed by the symmetric rotor eigenfunctions $S_{Jkm}(\varphi,\theta)e^{ik\chi}$[15] and any set of basis functions suitable to approximating the torsional wave functions.

Pickett also derived how the kinetic energy tensor elements are transformed by rotating to a new MFS with a LAM-dependent rotation.[14] Rotate the MFS by a rotation U. By saying that the MFS is rotated by U, we understand that the row of the unit vectors of the new MFS, $(\mathbf{E}_x,\mathbf{E}_y,\mathbf{E}_z)$, is related to that of the initial one, $(\mathbf{e}_x,\mathbf{e}_y,\mathbf{e}_z)$, by the transformation $(\mathbf{E}_x,\mathbf{E}_y,\mathbf{E}_z)=(\mathbf{e}_x,\mathbf{e}_y,\mathbf{e}_z)U$. Thus U^t transforms the column vectors $(a_{x,j},a_{y,j},a_{z,j})^t$ of the coordinates of the atoms, and one can find the relationships

$$I_{RR}\rightarrow U^t I_{RR} U, \tag{10}$$

$$\omega\rightarrow U^t(\omega-\omega_U), \tag{11}$$

$$\mu_{\tau\tau}\rightarrow\mu_{\tau\tau}, \tag{12}$$

where ω_U is the angular velocity vector defined by U according to

$$\Omega_U=\begin{pmatrix} 0 & -(\omega_U)_z & (\omega_U)_y \\ (\omega_U)_z & 0 & -(\omega_U)_x \\ -(\omega_U)_y & (\omega_U)_x & 0 \end{pmatrix}=-U\frac{\partial U^t}{\partial\tau}. \tag{13}$$

(Srictly speaking ω_U is not an angular velocity vector. Only $\omega_U d\tau/dt$, where $d\tau/dt$ is the time derivative of τ, is an angular velocity vector.)

The potential energy, $V(\tau)$, does not depend on the orientation of the MFS. Thus, the Hamiltonian in the rotated system takes the form

$$\begin{aligned}\hat{H}_U={}&\tfrac{1}{2}\hat{P}^t U^t \mu_{RR} U \hat{P}+\tfrac{1}{2}(\hat{p}'-\{\hat{P}^t U^t(\omega-\omega_U)\})\mu_{\tau\tau}\\ &\times(\hat{p}'-\{(\omega-\omega_U)^t U\hat{P}\})+V(\tau),\end{aligned} \tag{14}$$

with $\hat{P}=(\hat{P}_x,\hat{P}_y,\hat{P}_z)^t$ denoting the column vector of the components of the total angular momentum operator given in the new MFS, and

$$\hat{p}'=-i\hbar\left(\frac{\partial}{\partial\tau}\right)_{\varphi',\theta',\chi'}, \tag{15}$$

where the Euler angles φ',θ', and χ' define the orientation of the new MFS with respect to the LS.

Since the total angular momentum is conserved, $\hat{P}$ is related to $\hat{J}$ by

$$\hat{P}=U^t\hat{J}. \tag{16}$$

By substituting Eq. (16) into the expression of $\hat{H}_U$ and comparing the terms in the resulting Hamiltonian with those in $\hat{H}$ one finds the relationship

$$\hat{p}'=\hat{p}-\omega_U^t\hat{J}. \tag{17}$$

Equation (17) may be considered as a generalization of the Nielsen transformation.[5] By replacing $\hat{J}$ with $U\hat{P}$ and $\hat{p}$ with $\hat{p}'+\omega_U^t U\hat{P}$ in $\hat{H}$, $\hat{H}_U$ is obtained.

The angular momentum operator $\hat{P}$ satisfies the same commutation relations as $\hat{J}$:

$$\hat{P}\times\hat{P}=U^t\hat{J}\times U^t\hat{J}=U^t(\hat{J}\times\hat{J})=-i\hbar U^t\hat{J}=-i\hbar\hat{P}. \tag{18}$$

Therefore, the elements of $\hat{P}$ are given by the same mathematical expressions as those of the components of $\hat{J}$, but they are given in terms of the Euler angles φ',θ', and χ'. For a given value of total angular momentum quantum number, $P=J$, the matrix elements of the components of $\hat{P}$ calculated in the symmetric rotor basis $S_{Pkm}(\varphi',\theta')e^{ik\chi'}$ are the same as those of $\hat{J}$ calculated in the symmetric rotor basis $S_{Jkm}(\varphi,\theta)e^{ik\chi}$. The symmetric rotor eigenfunctions $S_{Pkm}(\varphi',\theta')e^{ik\chi'}$ give a suitable rotational basis for solving the Schrödinger equation of $\hat{H}_U$.

Similarly to $\hat{J}$ and $\hat{p}$ the operators $\hat{P}$ and $\hat{p}'$ commute:

$$\begin{aligned}[\hat{P},\hat{p}']&=[U^t\hat{J},\hat{p}-\omega_U^t\hat{J}]\\ &=U^t\hat{J}(\hat{p}-\omega_U^t\hat{J})-(\hat{p}-\omega_U^t\hat{J})U^t\hat{J},\\ i\hbar\frac{\partial U^t}{\partial\tau}\hat{J}+U^t[\omega_U^t\hat{J},\hat{J}]&=i\hbar\frac{\partial U^t}{\partial\tau}\hat{J}+i\hbar U^t\Omega_U\hat{J}\\ &=i\hbar\left(\frac{\partial U^t}{\partial\tau}+U^t\Omega_U\right)\hat{J}=\mathbf{0},\end{aligned} \tag{19}$$

where the last equality follows from Eq. (13).

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The results obtained in the above-presented discussions can be summarized as follows. The rotational-LAM Hamiltonian, $\hat{H}$, derived in an initial MFS can be given by Eq. (1), where the angular momentum operator, $\hat{J}$, and the momentum operator of the LAM, $\hat{p}$, satisfy the commutation relations given by Eqs. (7) and (9). The rotational-LAM Hamiltonian $\hat{H}_U$ that is given in a new MFS related to the initial MFS by a rotational transformation U can be obtained by replacing the angular momentum and momentum operators in the initial rotational-LAM Hamiltonian according to the rule

$$\hat{J} \rightarrow U\hat{P}, \tag{20}$$

$$\hat{p} \rightarrow \hat{p}' + \omega_U^t U \hat{P}. \tag{21}$$

This transformation preserves the commutation relations of the angular momentum and momentum operators. The symmetric rotor eigenfunctions expressed as functions of the Euler angles defining the orientation of the new MFS with respect to the LS give a useful rotational basis set for solving the Schrödinger equation of $\hat{H}_U$. The choice of the LAM basis depends on the actual boundary conditions and will be discussed shortly. The results obtained in this section are straightforward to extend to the case of more than one LAM.

III. THE INTERNAL-AXIS SYSTEM HAMILTONIAN

The IAS is obtained by rotating the initial MFS by a LAM dependent rotation D such that

$$\omega - \omega_D = \mathbf{0}. \tag{22}$$

Then, the Hamiltonian given in Eq. (14) simplifies to

$$\hat{H}_D = \tfrac{1}{2}\hat{P}^t D^t \mu_{RR} D \hat{P} + \tfrac{1}{2}\hat{p}' \mu_{\tau\tau} \hat{p}' + V(\tau). \tag{23}$$

As shown in Sec. II, $\hat{P}$ satisfies the commutation relation Eq. (18) and commutes with $\hat{p}'$.

An analytical expression of the matrix transforming to the IAS has been derived in Ref. 13 by employing the Floquet method:

$$D_{\alpha\beta} = \sum_{\gamma=-1}^{1} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \langle \alpha, n | \gamma \rangle e^{inM\tau} e^{-i\epsilon_\gamma \tau} \langle \gamma | \beta, m \rangle$$
$$(\alpha, \beta = x, y, z). \tag{24}$$

The basis set $\{|\alpha, n\rangle, \quad \alpha = x, y, z, \quad n = 0, \pm 1, \pm 2, \ldots, \pm \infty\}$ is the direct product of the Fourier basis and the basis set

$$|x\rangle = \frac{1}{\sqrt{2}}(-|1,1\rangle + |1,-1\rangle), \tag{25}$$

$$|y\rangle = \frac{i}{\sqrt{2}}(|1,1\rangle + |1,-1\rangle), \tag{26}$$

$$|z\rangle = |1,0\rangle, \tag{27}$$

where $|1,1\rangle, |1,-1\rangle$, and $|1,0\rangle$ are the complex spherical harmonics, $|J,m\rangle$, for $J=1$. $\epsilon_\gamma, \gamma = 1,0,-1$, $(\epsilon_1 > \epsilon_0 > \epsilon_{-1})$, are the three central eigenvalues of the Floquet operator,

$$\hat{\mathcal{F}} = \omega \cdot \hat{J} - i\frac{\partial}{\partial \tau}, \tag{28}$$

where $\hat{J}$ is an angular momentum operator satisfying $\hat{J} \times \hat{J} = i\hat{J}$, and $|\gamma\rangle, \gamma = 1,0,-1$ are the corresponding eigenfunctions. [Note that the imaginary i in $i\omega \cdot \hat{J}$ in Eq. (19) of Ref. 13 should be omitted.] Finally, the integer M denotes that the angular velocity vector ω calculated in the initial MFS is a $2\pi/M$ periodic function of τ. ($M=1$ was assumed in Ref. 13.)

The rotation matrix D can be factorized as

$$D = \mathcal{F}\boldsymbol{\epsilon}F_0^\dagger = (\mathcal{F}F_0^\dagger)(F_0\boldsymbol{\epsilon}F_0^\dagger) = (\mathcal{F}F_0^\dagger)\mathcal{R}, \tag{29}$$

where

$$\mathcal{F}_{\alpha\gamma} = \sum_{n=-\infty}^{\infty} e^{inM\tau} \langle \alpha, n | \gamma \rangle, \tag{30}$$

$$(F_0)_{\beta\gamma} = \sum_{m=-\infty}^{\infty} \langle \beta, m | \gamma \rangle, \tag{31}$$

$$\mathcal{R} = F_0 \boldsymbol{\epsilon} F_0^\dagger, \tag{32}$$

and, by making use of the properties $\epsilon_0 = 0$ and $\epsilon_1 = -\epsilon_{-1}$ of the central Floquet eigenvalues,

$$\boldsymbol{\epsilon} = \begin{pmatrix} e^{-i\epsilon_1\tau} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{i\epsilon_1\tau} \end{pmatrix}. \tag{33}$$

Superscript † denotes Hermitian conjugation.

The matrices $\mathcal{F}$ and F_0 are unitary (see Ref. 16). The matrix $\mathcal{R}$ is unitary, its determinant is equal to one, and its eigenvalue matrix is $\boldsymbol{\epsilon}$. The angular velocity vector $\omega \equiv \omega_{\mathcal{R}}$ defined by $\mathcal{R}$ according to an equation similar to Eq. (13) (except that transposition is replaced by Hermitian conjugation) is independent of the LAM coordinate. The orthogonal matrix Z

$$Z = \frac{1}{\|\omega\| \omega_{xy}} \begin{pmatrix} \omega_z & 0 & -\omega_{xy} \\ 0 & \|\omega\| & 0 \\ \omega_{xy} & 0 & \omega_z \end{pmatrix}$$
$$\times \begin{pmatrix} \omega_x & \omega_y & 0 \\ -\omega_y & \omega_x & 0 \\ 0 & 0 & \omega_{xy} \end{pmatrix}, \tag{34}$$

where $\|\omega\|$ denotes the length of ω and $\omega_{xy} = \sqrt{\omega_x^2 + \omega_y^2}$, transforms ω such that

$$Z\omega = (0,0,\|\omega\|)^t. \tag{35}$$

The rotation matrix $Z\mathcal{R}Z^t$ generates the angular velocity vector $(0,0,\|\omega\|)^t$. The rotation of angle $\|\omega\|\tau$ around the z axis, i.e.,

$$\mathcal{R}_z = \mathcal{R}_z(\|\omega\|\tau) = \begin{pmatrix} \cos\|\omega\|\tau & -\sin\|\omega\|\tau & 0 \\ \sin\|\omega\|\tau & \cos\|\omega\|\tau & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{36}$$

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also generates the angular velocity vector $(0,0,\|\omega\|)^t$ and, in general, so does $\mathcal{R}_z Q$, where Q is any τ independent unitary matrix. $Z\mathcal{R}Z^t$ must be equal to $\mathcal{R}_z Q$ with some appropriate Q.

The matrix ϵ can also be obtained by diagonalizing $\mathcal{R}_z(\epsilon_1\tau)$. Let $C^\dagger$ denote the corresponding eigenvector matrix. Then $\epsilon = C\mathcal{R}_z(\epsilon_1\tau)C^\dagger$ and $Z\mathcal{R}Z^t = ZF_0C\mathcal{R}_z(\epsilon_1\tau)C^\dagger F_0^\dagger Z^t$. By equating the latter matrix to $\mathcal{R}_z(\|\omega\|\tau)Q$ and rearranging one obtains

$$\mathcal{R}_z(\epsilon_1\tau) = C^\dagger F_0^\dagger Z^t \mathcal{R}_z(\|\omega\|\tau)QZF_0C. \tag{37}$$

Equation (37) cannot be satisfied unless the matrix ZF_0C is either a unit matrix or a matrix of z-rotation, and Q is either a unit matrix or a matrix of z-rotation with constant angle, τ_0.

Therefore,

$$Z\mathcal{R}Z^t = \mathcal{R}_z(\epsilon_1\tau) = \mathcal{R}_z(\|\omega\|\tau + \tau_0), \tag{38}$$

and

$$\|\omega\| = \epsilon_1 \tag{39}$$

and

$$\tau_0 = 0 \tag{40}$$

follow.

Thus, one can factorize D as

$$\begin{aligned} D &= (\mathcal{F}F_0^\dagger)\mathcal{R} = (\mathcal{F}F_0^\dagger Z^t)(Z\mathcal{R}Z^t)Z \\ &= (\mathcal{F}F_0^\dagger Z^t)\mathcal{R}_z Z = S\mathcal{R}_z Z, \end{aligned} \tag{41}$$

where Z is a rotational matrix independent of the LAM coordinate [see Eq. (34)], $\mathcal{R}_z$ is a rotational matrix around a z axis with angle $\epsilon_1\tau$ [see Eq. (38)], and $S = \mathcal{F}F_0^\dagger Z^t$ is a rotational matrix whose elements are $2\pi/M$ periodic functions of the LAM coordinate.

Now, let us rotate the IAS by Z^t. Then, by applying the rules derived in Sec. II, one finds that the IAS rotational-LAM Hamiltonian given in Eq. (23) is transformed into the Hamiltonian

$$\hat{H}_{S\mathcal{R}_z} = \hat{H}_{DZ^t} = \tfrac{1}{2}\hat{L}^t \mathcal{R}_z^t S^t \mu_{RR} S \mathcal{R}_z \hat{L} + \tfrac{1}{2}\hat{p}'\mu_{\tau\tau}\hat{p}' + V(\tau), \tag{42}$$

where $\hat{L} = Z\hat{P}$, $\hat{p}' = -i\hbar(\partial/\partial\tau)_{\varphi'',\theta'',\chi''}$, and the Euler angles φ'',θ'', and χ'' describe the orientation of the new MFS with respect to the LS. The new MFS is an IAS and the corresponding rotational-LAM Hamiltonian, $\hat{H}_{DZ^t}$, is an IAS Hamiltonian. They can also be obtained by rotating the initial MFS by $S\mathcal{R}_z$ and by transforming the rotational-LAM Hamiltonian given in Eq. (1).

Let the Euler angles φ',θ', and χ' describe the orientation (with respect to the LS) of the MFS obtained by rotating the initial MFS by S. The two sets of rotational coordinates, φ'',θ'', χ'' and φ',θ', χ' are related by

$$\varphi'' = \varphi', \tag{43}$$

$$\theta'' = \theta', \tag{44}$$

$$\chi'' = \chi' + \epsilon_1\tau. \tag{45}$$

For a given value of the total angular momentum quantum number L the symmetric rotor eigenfunctions $S_{Lkm}(\varphi'',\theta'')e^{ik\chi''}$ give a suitable rotational basis for solving the Schrödinger equation for $\hat{H}_{DZ^t}$. To choose an appropriate LAM basis one must consider that the rotational-LAM wave functions are invariant upon changing the value of the LAM coordinate by 2π. This boundary condition is of importance only for molecules where a 2π change of the LAM coordinate can actually take place, e.g., in molecules with internal rotation. With changing τ by 2π, the Euler angles φ', θ', and χ' can change only by an integer multiple of 2π since S is 2π periodic, but

$$\chi'' = \chi' + \epsilon_1\tau \rightarrow \chi'' + 2\pi n + 2\pi\epsilon_1, \tag{46}$$

where n is an integer number. Since ϵ_1 is, in general, not an integer, the usual direct product basis functions $S_{Lkm}(\varphi'',\theta'')e^{ik\chi''}\phi_n(\tau)$, where $\phi_n(\tau)$ are 2π periodic, do not satisfy the boundary condition required. One remedy is to use the nondirect product basis functions

$$S_{Lkm}(\varphi'',\theta'')e^{ik\chi''}e^{-ik\epsilon_1\tau}\phi_n(\tau). \tag{47}$$

Another, but only approximate, method to satisfy the boundary condition approximates the value of ϵ_1 by the ratio of two relative prime integers and introduces a new torsional variable.[17,13]

Since $\mathcal{R}_z^t S^t \mu_{RR} S \mathcal{R}_z$ is not $2\pi/M$ periodic it does not seem obvious how the molecular symmetry may be taken into account when solving the IAS rotational–internal–rotational Schrödinger equation given by Eq. (42).

A rotational-LAM Hamiltonian whose Schrödinger equation is significantly simpler to solve than that of the IAS Hamiltonian in Eq. (42) is obtained by rotating the IAS into a new MFS by the rotation $\mathcal{R}_z^t$.

IV. THE ρ-AXIS SYSTEM HAMILTONIAN

The rotation of the (new) IAS by $\mathcal{R}_z^t$ transforms the IAS Hamiltonian given in Eq. (42) into the Hamiltonian

$$\begin{aligned} \hat{H}_S = {} & \tfrac{1}{2}\hat{P}^t S^t \mu_{RR} S \hat{P} + \tfrac{1}{2}(\hat{p}'' - \epsilon_1\hat{P}_z)\mu_{\tau\tau}(\hat{p}'' - \epsilon_1\hat{P}_z) \\ & + V(\tau), \end{aligned} \tag{48}$$

where $\hat{P} = \mathcal{R}_z\hat{L}$ and $\hat{p}'' = -i\hbar(\partial/\partial\tau)_{\varphi',\theta',\chi'}$. The commutation relations are, as usual, $\hat{P}\times\hat{P} = -i\hbar\hat{P}$ and $[\hat{P},\hat{p}''] = \mathbf{0}$.

The basis set formed by the direct product of the symmetric rotor eigenfunctions $S_{Pkm}(\varphi',\theta')e^{ik\chi'}$ and a suitably chosen LAM basis set can be used to find the eigenpairs of $\hat{H}_S$ variationally. Unlike in the case of the IAS Hamiltonians, now all kinetic energy tensor elements can be expanded into a Fourier series of periodicity $2\pi/M$. The value of M depends on the actual permutation inversion symmetry and LAM dynamics of the molecule studied. To make full use of the symmetry properties, however, the LAM coordinate must be defined properly.[2]

The Hamiltonian $\hat{H}_S$ can also be obtained by rotating the initial MFS by S and transforming the Hamiltonian given in Eq. (1) accordingly. Our results show that S rotates the initial MFS into a new one, where the internal angular velocity

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vector due to the LAM coincides with the z axis and has constant magnitude. Thus, the new MFS has all the characteristic properties of the MFS derived for special cases of internal rotation and called the ρ-axis system.[8] The Hamiltonian in Eq. (48) is a generalization of the ρ-axis system Hamiltonians discussed in Refs. 5 and 8 and may be called the generalized ρ-axis system Hamiltonian or just the ρ-axis system Hamiltonian. It is a simple excercise to show that $\hat{H}_S$ reduces to the known special case ρ-axis system Hamiltonians derived in Ref. 5. Numerical results presented in Sec. V give additional evidence for the correctness of the ρ-axis system Hamiltonian given in Eq. (48).

V. A NUMERICAL EXAMPLE

All terms in $\hat{H}_S$ can be determined by first-principles calculations. One parameter appearing in $\hat{H}_S$, namely ϵ_1, also appears in the effective spectroscopic Hamiltonian (where it is denoted by ρ) employed in fitting the rotational-torsional spectrum of acetaldehyde. Unlike most fitting parameters, ϵ_1 is free of vibrational contributions. Therefore, the comparison of the theoretically determined value of ϵ_1 with that obtained by fitting to experimental data should show good agreement.

Details of our *ab initio* calculations of the torsional potential and molecular geometries along the minimum energy torsional path of acetaldehyde have been described in Ref. 2. By utilizing the results of these calculations, the angular velocity vector due to internal rotation has been calculated along the minimum energy torsional path in an initial MFS and found to depend on the torsional coordinate τ_1 defined in Ref. 2 as

$$\begin{aligned}\omega_x &= -0.000\,770\,373 \sin 3\tau_1 + 0.000\,015 \sin 6\tau_1 \\ &\quad - 3.731\,96\times 10^{-7} \sin 9\tau_1, \\ \omega_y &= -0.103\,831 - 0.001\,256\,83 \cos 3\tau_1, \\ \omega_z &= 0.313\,246 + 0.005\,137\,83 \cos 3\tau_1.\end{aligned} \tag{49}$$

(More about these calculations will be described along with results obtained by very high-level *ab initio* calculations in a forthcoming publication.[18]) Then, following the prescriptions of Ref. 13 ϵ_1 is calculated. The theoretically determined value of 0.3300 agrees very well with the spectroscopic values 0.3316 and 0.3291 taken from Ref. 4. The deviation is less than 0.5%. For comparison it is worth mentioning that a recent attempt[1] to calculate ϵ_1 (ρ) *ab initio* gave the value 0.3384, which is more than 2% off the experimental values.

VI. SUMMARY

A simple rule has been obtained to transform the rotational-LAM Hamiltonian when the molecule fixed system of axes is rotated by some rotation that may depend on the LAM coordinate. (The extension of this rule to the case of more than one LAM is straightforward.)

Then, a ρ-axis system rotational-LAM Hamiltonian, Eq. (48), has been derived. It applies to any molecule with any type of LAM. The matrix S transforming to the ρ-axis system and the strength of the LAM-z-rotation momentum coupling, i.e., the constant denoted traditionally by ρ, can be calculated by finding the three central eigenvalues and corresponding eigenfunctions of the Floquet operator given in Eq. (28). In fact, ρ is identical to the positive central eigenvalue, ϵ_1, of the Floquet operator. The LAM-z-rotation momentum coupling constant can also be obtained from analyzing experimental spectroscopic data. For the case of acetaldehyde, the theoretically derived value was found to be in excellent agreement with that obtained from spectral analysis.

The ρ-axis system rotational-LAM Hamiltonian, Eq. (48), augmented with small amplitude vibrational contributions[19] can be the starting point of the derivation of an effective rotational-LAM Hamiltonian suitable to fit spectroscopic data. In addition to fitting, the parameters in this effective Hamiltonian will be amenable to first-principles calculations, since they will be given as functions of the molecular geometry and potential energy surface parameters.

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